

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-059390

(43)Date of publication of application : 04.03.1994

(51)Int.Cl.

G03C 1/79  
C07C 69/738

(21)Application number : 04-211725

(71)Applicant : NEW OJI PAPER CO LTD

(22)Date of filing : 07.08.1992

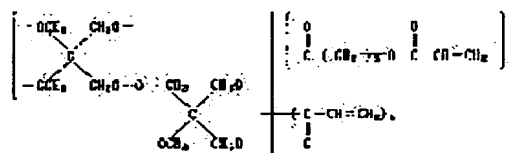
(72)Inventor : KOBAYASHI MASASHI  
TANAKA CHIEKO  
MIURA TAKAHARU

## (54) SUBSTRATE FOR PHOTOGRAPHIC PRINTING PAPER

## (57)Abstract:

PURPOSE: To provide a substrate for photographic printing paper not causing yellowing at the time of development, suppressing fog after storage and preventing the cracking of the surface resin layer.

CONSTITUTION: A surface resin layer based on an electron beam-curing resin is formed on the front side of a paper base by coating and curing and a resin backing layer is formed on the rear side. The surface resin layer has at least one inner resin layer having relatively low crosslinking density and the outermost resin layer having relatively high crosslinking density and contg. an unsaid. org. compd. represented by the formula (where (a) is 2 or 3, (b) is 3 or 4 and a+b=6). The objective substrate for photographic printing paper is obtd.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

## • NOTICES •

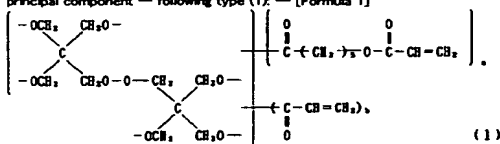
JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

[Claim(s)]

[Claim 1] The surface resin spreading hardening layer which consists of an electron ray hardened material of the partial saturation organic compound constituent which contains the partial saturation organic compound which it is formed the paper base which contains natural pulp as a principal component, and on the 1 front face, and can be hardened by electron beam irradiation as a principal component, the outermost layer of said surface resin layer to which said surface resin spreading hardening layer has the laminated structure more than two-layer, and should touch a photographic-emulsion layer including the rear-face resin enveloping layer which is formed on the opposite side of said paper base, and contains film plasticity synthetic resin as a principal component — following type (1): — [Formula 1]



(但し、上記式(1)において、aは2または3の整数を表わし、

bは3又は4の整数を表わし、aとbとの和は6である。)

The base material for the photographic printing papers characterized by being the electron ray hardened material of the partial saturation organic compound constituent containing at least one sort of electron ray hardenability partial saturation organic compounds which are alike and are expressed more.

[Translation done.]

## \* NOTICES \*

JPO and NCIPJ are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the base material for the photographic printing papers. Furthermore, it states in detail, this invention does not have generating of fogging at the time of the mothball when controlling yellowing of the resin paint film by the development, and maintaining sufficient flexibility, and making it the photographic printing paper, or relates to few base material ingredients for the photographic printing papers.

[0002]

[Description of the Prior Art] Conventionally, the polyolefin covering base material which covered polyolefin resin to both sides of the base which consists of paper, and was manufactured as a base material for the photographic printing papers has been used widely. Since processing liquid cannot permeate easily into a base material during development and fixing processing, and such a base material has the advantage that rinsing time amount and the drying time are shortened sharply for this reason, as compared with a baryta paper, since a polyolefin enveloping layer is hydrophobicity, and it does not have osmosis of the processing liquid to a paper base, telescopic motion of the base material itself is controlled and it has the advantages, such as having the outstanding dimensional stability.

[0003] Although inorganic white pigments like a titanium dioxide are mixed by such polyolefin resin enveloping layer of a base material for the purpose of improvement in obliterating power or resolving power, such a pigment has the bad dispersibility to the inside of resin, and in a melting extrusion process, it foams to it by the volatile component contained in a pigment, and there are problems, such as generating the film crack of an enveloping layer, in it. For this reason, the pigment content in an enveloping layer cannot be raised to level sufficient for improvement in the above-mentioned obliterating power or resolution. When using a titanium dioxide, speaking generally, it is difficult to add this to an enveloping layer with about 20% of the weight or more of an addition. Therefore, the photographic printing paper obtained using such a base material for the photographic printing papers was not able to say it as what can be enough satisfied in image sharp nature.

[0004] The so-called electron ray hardenability resin which becomes recent years and consists of a resin constituent which can be hardened by electron beam irradiation is applied to a base material, and the base material for the photographic printing papers which has the electron ray hardening resin spreading layer which gave and hardened electron beam irradiation to this is proposed (for example, JP.60-17104.B, JP.60-17105.B, JP.57-49946.A, etc.). Since heating fusion of the resin constituent is not carried out at an elevated temperature in case a spreading layer is formed according to this approach, a pigment content can be made to increase to 20-80% of the weight, therefore, compared with the polyolefin resin covering photographic printing paper, the image sharp nature of the photographic printing paper obtained using such a base material is boiled markedly, and is improving.

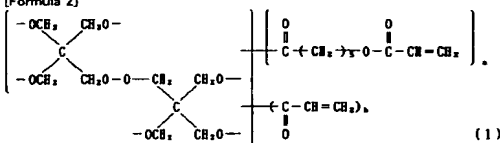
[0005] However, the photographic printing paper which applied the photograph sensitization layer on the electron ray hardening resin spreading layer hardened by electron beam irradiation, and was manufactured in a development process, adsorb on an electron ray hardening resin

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.ejie](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejie)

2006/11/30

the laminated structure more than two-layer, and succeeded in solution of the above-mentioned technical problem by using the partial saturation organic compound which can be hardened by specific electron beam irradiation at least for an outermost resin spreading layer, and completed this invention.

[0013] The paper base with which the base material for the photographic printing papers of this invention contains natural pulp as a principal component, The surface resin spreading hardening layer which consists of an electron ray hardened material of the partial saturation organic compound constituent which contains the partial saturation organic compound which it is formed on the 1 front face, and can be hardened by electron beam irradiation as a principal component, the outermost layer of said surface resin layer which said resin spreading hardening layer has the laminated structure more than two-layer, and touches a photographic-emulsion layer including the rear-face resin enveloping layer which is formed on the opposite side of said paper base, and contains film plasticity synthetic resin as a principal component — following type (1): —



(但し、上記式 (1) において、a は 2 または 3 の整数を表わし、

b は 3 または 4 の整数を表わし、a と b の和は 5 である。)

It is the object characterized by being the electron ray hardened material of the partial saturation organic compound constituent containing at least one sort of electron ray hardenability partial saturation organic compounds which are alike and are expressed more.

[0014]

[Function] The configuration of this invention and an operation are explained below. The photographic printing paper manufactured from the base material which generally applied the commercial electron ray hardenability compound constituent to the paper base which uses natural pulp as a principal component, irradiated the electron ray at this, formed the electron ray hardening resin spreading layer, and was obtained has the so-called problem of the development which colors it yellow after a development as mentioned above, and yellowing. Although the cause of yellowing is not completely clear, in the development process, the developing agent in the development chemical for photographs carries out an adsorption residual at a base material, and it is thought that it oxidizes and coloring is caused.

[0015] In order to prevent yellowing, for that purpose, it is [that what is necessary is just to decrease adsorption of a developing agent] effective to increase the crosslinking density of the paint film of a base material, for this reason means, such as making [many] the loadings of making the amount of exposure electron rays for stiffening a resin constituent into a high dose, a polyfunctional partial saturation organic compound monomer, or oligomer and blending many comparatively small partial saturation organic compounds of molecular weight, are effective. However, when electron-beam-irradiation dosage was made high, each of these approaches increased fogging at the time of the mothball when considering as printing paper, and it not only degrades the flexibility of a paint film, but they had the fault of making a stencil paper base discolor yellow by the impact of electron beam irradiation in addition further.

[0016] As a result of this invention persons' examining many things about this point, the surface resin spreading layer which contains the partial saturation organic compound which it is formed

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.ejie](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejie)

2006/11/30

spreading layer, and the development chemical for photographs remains. It is known that the development which colors yellow after a development, i.e., yellowing, may occur, the concentration of fogging may increase to extent which cannot be disregarded as a product if a development is further performed to this after the preservation passage of time, or sensibility may change. Moreover, in one side, a paint film is hard, flexibility is missing, and it is also known that there are troubles, such as a chip box crack.

[0006] In order to solve the problem of the above-mentioned fogging, the various improvement approaches are proposed. For example, the method of preparing the enveloping layer of polyethylene on an electron ray hardening resin spreading layer is indicated as a means to control the sensibility change at the time of preservation by JP.1-21495.B. However, in this approach, if the enveloping layer of polyethylene is not made quite thick, the effectiveness of fogging reduction is inadequate, therefore it has the trouble at the sacrifice of the improvement in image sharp nature which is the greatest merit when using an electron ray hardening technique.

[0007] Moreover, the approach of controlling change of photographic sensitivity is proposed by JP.60-144738.A by arranging a filter layer between stencil paper and an electron ray hardening resin spreading layer. However, when the charge of shielding layer formation material currently indicated here is used, about the point of the fogging prevention at the time of a mothball, it is still inadequate.

[0008] The specific electron ray hardenability polymer for prevention of fogging and yellowing, flexible-izing of a paint film, etc., Using an electron ray hardenability monomer Or for example, JP.59-124338.A (acrylic ester monomer), JP.60-70446.A (urethane resin which has a double bond), and JP.61-201241.A (diacrylate —) A thoria chestnut rate, epoxidation acrylate, JP.61-236547.A (tetra-acrylic ester), Although proposed by JP.62-61049.A (hexa acrylate ester), JP.62-109046.A (polybutadiene content resin), and JP.2-47.A (acrylate ester of the acrylic-acid polymer addition product of polyhydric alcohol) Even if it uses these electron ray hardenability monomers, it has not yet resulted in sufficient solution in question.

[0009] About yellowing of the paint film by the above-mentioned developer, the relation to the flexibility of a paint film to fogging concentration is, and it is known that the inclination which conflicts to quantity of radiation is shown. That is, although yellowing of the paint film by the developer is low suppressed when a high exposure dose is used, fogging becomes high and there is an inclination for the flexibility of a paint film to deteriorate. Moreover, the paper durability of a paper base and deterioration of quality of paper will also be caused. On the other hand, with a low exposure dose, although generating of fogging is controlled and the flexibility of a paint film is secured to some extent, the yellowing increases remarkably and has the inclination for paint film physical properties, such as an adhesive property and film reinforcement, to also get worse further.

[0010] Therefore, it is that it is very important to develop the presentation of a surface resin spreading hardening layer which is not accompanied by the paper durability of fogging, flexibility, and a paper base and deterioration of quality of paper even if it irradiates sufficient amount of electron rays required for paint film bridge formation with selection of an electron ray hardenability organic unsaturated compound, in order not to worsen paint film physical properties and to improve xanthochroism, and the formation approach in order to cancel all the above-mentioned troubles that it is simultaneous and effectively.

[0011]

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned trouble of the conventional technique, is excellent in surface smooth nature, holds a high water resisting property, moreover, there is no increment in fogging generating by the development also after the preservation passage of time, it has paint film flexibility, also tends to control xanthochroism to coincidence, and tends to offer the suitable base material for the photographic printing papers to manufacture the photographic printing paper which has the paper durability of a paper base, and the outstanding photograph property with little degradation of quality of paper.

[0012]

[Means for Solving the Problem] this invention persons made the surface resin spreading layer

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.ejie](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejie)

2006/11/30

on 1 front face of a paper base, and can be hardened by electron beam irradiation as a principal component is made into the laminated structure more than two-layer as mentioned above. And it found out that these problems were effectively solvable by using for the spreading layer of an outermost layer the partial saturation organic compound which can be hardened by the high electron beam irradiation of crosslinking density at least, i.e., the constituent containing at least one sort of partial saturation organic compounds of a formula (1). That is, in the development of the photographic printing paper, when the base material outermost part which contacts a developer through a photographic-emulsion layer was formed by the resin spreading layer which has a viaduct consistency and crosslinking density arranged a comparatively low flexible resin spreading layer to the inside which does not touch a developer, it succeeded in making coincidence improve flexibility and xanthochroism.

[0017] The base material of this invention which has the laminated structure which consists of two or more above layers The coating liquid for at least one-layer inside layers which contains an electron ray hardenability partial saturation organic compound as a principal component is applied to at least 1 front face of the paper base which contains natural pulp as a principal component. Furthermore, on the coating liquid layer for inside layers, it can apply sentimentally and the coating liquid for outermost layers which contains an electron ray hardenability partial saturation organic compound as a principal component can be manufactured by sentiment-on and the 1st approach of irradiating an electron ray at this multistory object.

[0018] Moreover, as the 2nd approach, the coating liquid for inside layers is applied, the 1st electron ray is irradiated, and a base material can be manufactured by irradiating the 2nd electron ray to the coating liquid for outermost layers on this inside layer at sentiment-on and the multistory object which applied in a businesslike manner and was acquired.

[0019] As the 3rd approach, contrary to the 2nd approach of the above, moreover, the coating liquid for outermost layers it applies on smooth front faces, such as a proper molding side, for example, a metal drum, plastics, or process paper. The transfer laminating of this outermost hardening resin layer can be carried out to the wet spreading side of the paper base which gave the 1st electron beam irradiation to this coating liquid layer for outermost layers, next applied the coating liquid for inside layers, and a base material can be manufactured by carrying out the 2nd electron beam irradiation to this multistory object.

[0020] Furthermore, a base material can be manufactured as the 4th approach by carrying out the sentiment-on wet laminating of the coating liquid layer for inside layers on a paper base, and the coating liquid layer for outermost layers by transfer coating, irradiating an electron ray at this multistory object, and carrying out hardening coalesce.

[0021] carry out for taking which approach — carrying out division spreading of the spreading layer more than two-layer makes it possible to improve the degree of freedom of spreading in heavy spreading, to improve spreading nature, and to give a function original with each class. Moreover, when performing transfer coating using a smooth molding base front face, the smooth nature of the front face of the base material obtained improves much more.

[0022] carry out for adopting what kind of the method of application by this invention — the surface resin spreading hardening layer containing an electron ray hardenability partial saturation organic compound is divided at least more than two-layer, and it becomes possible to raise the spreading nature and smooth nature. Moreover, it becomes possible to use the partial saturation organic compound of the inside spreading layer of a surface spreading layer, and an outermost spreading layer properly, to separate the function, and to decrease yellowing and fogging, and to increase the flexibility of a paint film by this invention.

[0023] Furthermore, it becomes possible to divide and give the amount of electron beam irradiation to an inside spreading layer and an outermost spreading layer by this invention, and to decrease yellowing and fogging, and to increase the flexibility of a paint film. Furthermore, this invention enables it to obtain the surface resin hardening layer which has a smooth front face by forcing an outermost spreading layer on a molding side.

[0024] in two or more layer laminating base material of this invention, in order to make the flexibility of the surface resin spreading hardening film, yellowing, and fogging prevention balance, carry out for adopting which the method of application — it is desirable to control the coverage

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.ejie](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejie)

2006/11/30

of an outermost layer and an inside layer in a suitable amount the 1st. after { namely, } the coverage of the whole surface resin spreading hardening layer hardening — setting — 5 g/m<sup>2</sup> the above — 50 g/m<sup>2</sup> it is the following — desirable — 15 g/m<sup>2</sup> — 50 g/m<sup>2</sup> it is — things are more desirable. If it does in this way, the good smooth nature as a base material for the photographic printing papers, concealment nature, and resolution will be acquired.

[0025] the function of an outermost layer is demonstrated — making — the flexibility of a paint film, and yellowing — in order to secure prevention — the coverage after the hardening — 0.5 g/m<sup>2</sup> the above — 15 g/m<sup>2</sup> making it below — desirable — 1 g/m<sup>2</sup> the above — 5 g/m<sup>2</sup> it is more desirable to make it below. the weight of this outermost layer — 0.5 g/m<sup>2</sup> the smooth nature of the base material obtained when not filling, and yellowing — tightness — inadequate — becoming — it — 20 g/m<sup>2</sup> When exceeding, the flexibility of a paint film becomes inadequate, and it becomes easy to generate a chip box crack.

[0026] In this invention, the outermost resin layer which forms the spreading side of a photographic emulsion among surface resin spreading hardening layers is formed from the electron ray hardenability resin constituent containing the partial saturation organic compound of the formula (1) which can form a viaduct resin layer. although this invention persons proposed using the electron ray hardenability compound which has four or more functional groups as the partial saturation organic compound for outermost layers concerned previously — the inside of it — the partial saturation organic compound of a formula (1) — especially — yellowing — it found out that it was effective in making tightness and the flexibility of the hardening film balance.

[0027] In the compound of a formula (1), it found out that especially the caprolactone denaturation acryloyl radical content hexa acrylate whose a the sum total of a and b shows the effectiveness excellent in 6, i.e., 5 functional-group content acrylate, and is 2 or 3 therefore whose b is 3 or 4 was excellent. In the partial saturation organic compound constituent which forms an outermost layer, although that the monomer of electron ray hardenability etc. dilutes does not interfere, as for the partial saturation organic compound of a formula (1), it is desirable that the partial saturation organic compound of a formula (1) is contained to the total weight of the electron ray hardenability partial saturation organic compound contained in this constituent with at least 75% of the weight or more of content. if this content becomes less than 75% of the weight — yellowing — it may become difficult to attain tightness and the flexibility of the hardening film with sufficient balance

[0028] if it is what can form a low bridge formation resin layer as an electron ray hardenability organic compound used for the resin spreading layer located inside among surface resin spreading hardening layers in this invention — a monomer — even when it is independent — oligomer — it may be independent, they may be blended, and there is especially no limitation also in the class of compound. About this inside layer, since there is no fear of yellowing by the development and it is not necessary to raise crosslinking density especially, it can be used, being able to choose the resin which was excellent in flexibility.

[0029] In this invention, the surface resin spreading hardening layer formed on 1 front face of a paper base is formed from the resin constituent which contains other additives if needed including the partial saturation organic compound which can be hardened with an electron ray, and mixture with white pigments as a principal component. In this invention, although especially the electron ray hardenability partial saturation organic compound used for formation of an inside layer is not limited by the number of functional groups etc., in order to give high flexibility, it is advantageous [ an organic compound ] especially from the purpose of this invention to use the compound of less than four organic functions which gives low crosslinking density.

[0030] The unsaturated compound used in order to form the surface resin spreading hardening layer of this invention can be chosen for example, from the following compound.

(1) The acrylate compound (2) aliphatic series of the alcohol and the polyalkylene glycol of aliphatic series, an alicyclic group, and aroma aliphatic series. Although alkylene oxide was made to add to the alcohol of an alicyclic group and aroma aliphatic series, an acrylate compound (3) poly acryloyl alkyl phosphoric ester (4) carboxylic acid. The resultant of the resultant (7) epoxy compound of polyol, resultant (5) isocyanate with an acrylic acid, polyol, and a resultant (6) epoxy compound with an acrylic acid and an acrylic acid, polyol, and an acrylic acid [0031] If this

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi\\_ejpe](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejpe)

2006/11/30

irradiated by the outermost layer, it is more desirable for the above-mentioned purpose.

[0038] The effectiveness of this invention is especially demonstrated advantageously by adopting the 3rd above-mentioned approach. That is, since the electron-beam-irradiation dosage to a paper base can be stopped low according to the 3rd approach, it is possible to control discoloration of the paper base by electron beam irradiation, and it is possible to also control fogging at the time of the mothball which originates in the electron beam irradiation to a paper base further.

[0039] Although that method cannot be limited and electron-beam-irradiation equipments, such as a van DEGRAUF mold scanning method, a doubles Canning method, and a curtain beam method, can be used especially as an electron ray accelerator used for electron beam irradiation, it is comparatively cheap also in this and the thing of the curtain beam method with which high power is obtained is used effectively. It is desirable that it is 100-300kV, as an absorbed dose, as for the acceleration voltage in the case of electron beam irradiation, it is desirable that it is 0.1 - 6Mrad, and especially its 0.2 - 4Mrad is desirable.

[0040] The oxygen density in the ambient atmosphere at the time of electron beam irradiation is 500 ppm. It is desirable that it is the following. An oxygen density is 500 ppm. When it exceeds, oxygen may work as a retarder of a polymerization reaction and hardening of a resin constituent may become inadequate. moreover, in the case of the 3rd approach of a transfer system of performing the 2nd electron beam irradiation after laying a non-hardened layer on top of the hardening paint film which received the 1st electron beam irradiation. Although electron ray hardenability coating liquid does not need to touch direct air into electron beam irradiation, therefore it is not necessary to reduce especially the oxygen density in the ambient atmosphere at the time of electron beam irradiation, it is the purpose which controls ozone generating by electron beam irradiation. Or, of course, it is convenient for using inert gas for the purpose, such as cooling of the window which generates heat in case an electron ray passes.

[0041] As film plasticity synthetic resin used for forming the rear-face resin enveloping layer of this invention, the polyolefin resin used for manufacture of the conventional base material for the photographic printing papers or the above-mentioned electron ray hardening resin can be used.

[0042] It can choose out of at least two sorts of mixture of homopolymers, such as ethylene and alpha olefins, for example, a propylene etc., at least two sorts of copolymers of said olefin, and these various polymers etc. as polyolefin resin for forming a rear-face resin enveloping layer. Especially desirable polyolefin resin is low density polyethylene, high density polyethylene, straight chain mold low density polyethylene, and such mixture. Although there is especially no limit in the molecular weight of polyolefin resin, the thing of the range of 20,000-200,000 is usually used. In polyolefin resin, a small amount of antioxidant and lubricant may be added if needed. In order to form a rear-face resin enveloping layer using polyolefin resin, the usual melting extrusion covering can be used.

[0043] Moreover, a rear-face resin enveloping layer can also be made to form with an electron ray hardenability partial saturation organic compound. For that, all the compounds used for formation of the above-mentioned surface resin spreading layer can be used. Furthermore, the formation approach of a rear-face resin enveloping layer is also good as multilayer structure as well as the case of the above-mentioned surface resin enveloping layer. Although there is especially no limit in the weight of a rear-face resin enveloping layer, generally it is 10 - 40 g/m<sup>2</sup>. It is desirable that it is in the range.

[0044] As a paper base used for this invention, it is usually 50 - 300 g/m<sup>2</sup>. It has a basis weight and paper with a smooth front face is used. Such paper can be chosen from all the things generally used for the base material for the photographic printing papers. Generally as natural pulp which forms a paper base, what uses softwood pulp, hardwood pulp, needle-leaf tree broad-leaved tree mixing pulp, etc. as a principal component is used widely. Moreover, a loading material can be made to contain in a paper base.

[0045] When printing paper is manufactured from the base material of this invention, it is effective to make magnesium compounds, such as a magnesium hydroxide, a magnesium oxide, and magnesium salt, contain in a paper base in order to prevent fogging generated at the time of the mothball. Furthermore, additives, such as the sizing compound generally used for paper

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi\\_ejpe](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejpe)

2006/11/30

is described concretely, as an electron ray hardenability partial saturation organic compound Polyoxyethylene epichlorohydrin denaturation bisphenol A diacrylate, Dicyclohexyl acrylate, epichlorohydrin denaturation polyethylene-glycol diacrylate, 1,6-hexanediol diacrylate, hydronium KISHIBI valine acid ester neopentyl glycol diacrylate, Nonyl phenoxy polyethylene-glycol acrylate, ethyleneoxide denaturation phenoxy-ized phosphoric-acid acrylate, Ethyleneoxide denaturation phthalic-acid acrylate, polybutadiene acrylate, KAPUORAKUTAN denaturation tetrahydrofurfuryl acrylate, tris (carboxyethyl) isocyanurate, Trimethylolpropane triacrylate, a pentaerythritol thoria chestrut rate, Pentaerythritol tetraacrylate, polyethylene-glycol diacrylate, 1, 4-butadiene diol diacrylate, neopentyl glycol diacrylate, neopentyl glycol denaturation trimethylol propane diacrylate, etc. can be raised. These compounds are independent or can be used combining the two or more sorts.

[0032] In this invention, the surface resin spreading hardening layer formed on 1 front face of a paper base contains other additives if needed by making into a subject the partial saturation organic compound which can be hardened with an electron ray as mentioned above, and mixture with white pigments. That is, it is desirable to make a surface resin spreading hardening layer contain white pigments for the purpose of the sharp disposition top when considering as printing paper. Although a titanium dioxide (an anatase mold and rutile mold) is mainly used as white pigments, to others, each of a barium sulfate, a calcium carbonate, an aluminum oxide, zinc oxides, magnesium oxides, magnesium hydroxides, etc. is usable.

[0033] As for the content of white pigments, it is desirable that it is 20 - 80% of the weight of the total-solids weight of a surface resin spreading hardening layer. When the sharp nature of the photograph on the printing paper obtained is not sometimes enough if the content becomes less than 20% of the weight, and it exceeds 80% of the weight, the flexibility of the resin spreading layer obtained may fall and a film crack may be produced.

[0034] In order to distribute white pigments in the above electron ray hardenability partial saturation organic compounds, 3 roll mills (three roll mill), 2 roll mills (two roll mill), a cow loess dissolver, a homomixer, a Sand grinder, a planetary mixer, an ultrasonic disperser, etc. can be used.

[0035] Moreover, as the method of application of a resin constituent for a molding side front face or a paper base front face, any, such as the bar coat method, the blade coat method, the squeeze coat method, the Ayr knife coat method, the roll coat method, the gravure coat method, and the transfer coat method, may be used, for example. Furthermore, for this reason, a fountain coating machine or a slit-die coating-machine method can also be used. When using especially the front face of a metal drum as a molding side, the roll coat method or the offset gravure coat method which uses a rubber covered roll from the consideration for not attaching a blemish to a molding side front face is used, and non-contact type a fountain coating machine and the slit-die coating-machine method are used further advantageously.

[0036] There are four kinds of approaches among the formation approaches of a surface resin spreading hardening layer of having a laminated structure more than two-layer in this invention. Like the above-mentioned. Although it is possible to include the partial saturation organic compound of a formula (1) in an outermost coating liquid layer as a principal component even when using any of four kinds of this approach, according to the method of application used, spreading sequence and the amount of electron beam irradiation change automatically.

[0037] By including the partial saturation organic compound of a formula (1) in an outermost layer, the crosslinking density of an outermost layer can be raised and yellowing can be prevented by it. Moreover, in order to form an inside layer, the low unsaturated compound of crosslinking density can be applied and the flexibility of the whole paint film can be maintained to the sufficient level. Since a lot of electron rays are irradiated in hardening of an inside layer in the 2nd approach, this approach is not desirable in order to form the high inside layer of flexibility. In the 1st and the 4th approach, since the count of electron beam irradiation is all 1, these approaches are desirable approaches, in order to obtain a flexible inside layer. However, in order to obtain the good outermost layer of smooth nature, the 3rd and 4th approaches which have adopted the transfer coating method for using a smooth shaping front face are desirable. Especially the 3rd approach is the transferring method, and since a lot of electron rays are

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi\\_ejpe](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejpe)

2006/11/30

manufacture, a fixing agent, a paper reinforcing agent, a loading material, an antistatic agent, a pH regulator, a pigment, and a color, may be blended with the paper base. Furthermore, a surface sizing compound, a surface paper durability agent, a pigment, a color, an antistatic agent, etc. may be suitably applied to a front face.

[0046]

[Example] Although the following example explains the configuration and effectiveness of this invention further, of course, the range of this invention is not restricted to these modes.

[0047] Example 1 basis weight of 180g/m<sup>2</sup> Surface activity-ized processing by corona discharge is performed on the rear face of a paper base, melting extrusion covering of polyethylene resin is performed on it, and the amount of covering is 30 g/m<sup>2</sup>. The rear-face resin enveloping layer was formed, the outermost front face which has the following presentation independently — the electron ray hardenability organic compound-white-pigments mixing constituent for resin spreading hardening stratification (constituent 1) was prepared.

[0048]

Constituent 1 \*\* Part Loadings Caprolactone denaturation dipentaerythritol hexa 54 weight sections Acrylate (two caprolactone denaturation A chestrut roll radical content, trademark: KAYARAD DPCA-20, Nippon Kayaku make)

1, 9-nonane diol diacrylate monomer Six weight sections (a diluent, a trademark: new frontier L-C9A, Dai-Ichi Kogyo Seiyaku make)

Titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) the mixing ratio of the 40 weight \*\*\* above-mentioned caprolactone denaturation hexa acrylate and a diluent monomer -

- rate: — 90 to 10 [0049] Mixed distribution of the mixture of the above-mentioned component was carried out with the paint conditioner for 1 hour, and the electron ray hardenability constituent was prepared. A wire bar is used on the front face of the metal plate which gave chrome plating which uses this constituent as a molding side, it applies so that the coverage after hardening may become 3 g/m<sup>2</sup>, and the electron ray was irradiated on condition that acceleration voltage:175Kv and absorbed-dose:2Mard, and this coating liquid layer was made to harden this spreading layer.

[0050] Independently, the following electron ray hardenability organic compound-white-pigments mixing constituent for inside layers (constituent 2) was prepared.

[0051]

Constituent 2 \*\* Part Loadings Electron ray hardenability resin (the mixture of 2 functional-group content oligomer and a diluent 60 weight section monomer, trademark:SN-5X 2671, Samponko make)

Titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) 40 weight sections [0052] Mixed distribution of the mixture of the above-mentioned component was carried out with the paint conditioner for 1 hour, and the electron ray hardenability constituent was prepared. A wire bar is used for this constituent on the front face of the above-mentioned paper base, and the coverage after hardening is 25 g/m<sup>2</sup>. It applied so that it might become, and this coating liquid layer was irradiated by acceleration voltage:175Kv from the tooth back of superposition and a paper base at the spreading hardening layer on the above-mentioned metal plate molding side, the electron ray was irradiated on condition that absorbed-dose:2Mard, and the multistory object was hardened and pasted up. Next, the layered product obtained from the metal plate molding side according to the above-mentioned process was exfoliated, and the base material for the photographic printing papers was created.

[0053] In order to test the xanthochroism by the development of the obtained base material for the photographic printing papers, the development which uses a DASUTO auto-processor (trademark: RCP20, product made from DASUTO) was presented with the sample offering base material. In order to evaluate the xanthochroism of the sample offering base material by which the development was carried out, according to TAPPI-T524 (1979 editions) "a Lab measuring method", b value before and behind a development was measured, and it evaluated considering the value (delta b value) which lengthened b value before a development from b value after a development as an index of xanthochroism. An evaluation result is shown in Table 1. Although less than 1.0 thing is [ delta b value ] practical, practical use is not borne or more by 1.0. A test

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi\\_ejpe](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejpe)

2006/11/30

result is shown in Table 1.

[0054] Evaluation of flexibility carried out the surface resin spreading layer of a sample offering base material outside, was twisted around the round bar with a diameter of 0.1cm, and carried out visual evaluation of the entering condition of cracking. The three-stage made into one point estimated what has broken that to which that it was not cracked at all was cracked three points and a little two points. Although the thing of three points and two points is practical, the thing of one point is not borne at practical use. A test result is shown in Table 1.

[0055] The base material for the photographic printing papers was produced like example 2 example 1. However, in said constituent 1, the constituent 3 was prepared having used the mixed ratio of said caprolactone denaturation hexa acrylate and diluent monomer as 75 to 25, and this was used instead of the constituent 1. The test result performed like the example 1 is shown in Table 1.

[0056] The base material for the photographic printing papers was produced like example 3 example 1. However, the electron ray hardenability organic compound-white-pigments mixing constituent for outermost layers of the following presentation (constituent 4) was prepared independently, and this was used instead of the constituent 1.

[0057] Constituent 4 \*\* Part Loadings Caprolactone denaturation dipentaerythritol hexa 54 weight sections Acrylate (three caprolactone denaturation acryloyl radical content, trademark :KAYARAD DPCA-30, Nippon Kayaku make) 1, 9-nonane diol diacrylate monomer Six weight sections (a diluent, a trademark: new frontier L-C9A, Dai-ichi Kogyo Seiyaku make)

titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) 40 weight \*\*\*\* — the mixing ratio of said caprolactone denaturation hexa acrylate and diluent monomer — rate: — the result of the test performed like 90 to 10 examples 1 is shown in Table 1.

[0058] The base material for the photographic printing papers was produced like example 4 example 3. However, in the constituent 1, the constituent 5 was prepared having used the mixed ratio of said caprolactone denaturation hexa acrylate and diluent monomer as 75 to 25, and this was used instead of the constituent 1. The result of the test performed like the example 1 is shown in Table 1.

[0059] The base material for the photographic printing papers was produced by the same actuation as example of comparison 1 example 1. However, the electron ray hardenability organic compound-white-pigments mixing constituent for outermost layers of the following presentation (constituent 6) was prepared independently, and this was used instead of the constituent 1.

[0060] Constituent 6 \*\* Part Loadings Pentaerythritol hexa acrylate 54 weight sections (caprolactone denaturation acryloyl radical nothing, a trademark: the beam set 700 and product made from the Arakawa chemistry)

1, 9-nonane diol diacrylate monomer Six weight sections (a diluent, a trademark: new frontier L-C9A, Dai-ichi Kogyo Seiyaku make)

Titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) The ratio of 40 weight \*\*\*\* hexa acrylate and the monomer for dilution: The result of the test performed like 90 to 10 examples 1 is shown in Table 1.

[0061] The base material for the photographic printing papers was produced like the example 1 of example of comparison 2 comparison. However, in the constituent 6, the constituent 7 was prepared having used the ratio of said hexa acrylate and diluent monomer as 75 to 25, and this was used instead of the constituent 6. The result of the test performed like the example 1 is shown in Table 1.

[0062] The base material for the photographic printing papers was produced like example of comparison 3 example 1. However, the electron ray hardenability organic compound-white-pigments mixing constituent for outermost layers of the following presentation (constituent 8) was prepared independently, and this was used instead of the constituent 1.

[0063] Constituent 8 \*\* Part Loadings Caprolactone denaturation dipentaerythritol hexa 54 weight

sections Acrylate (six caprolactone denaturation acryloyl radical content, trademark :KAYARAD DPCA-60, Nippon Kayaku make)

1, 9-nonane diol diacrylate monomer Six weight sections (a diluent, a trademark: new frontier L-C9A, Dai-ichi Kogyo Seiyaku make)

Titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) The mixed ratio of the 40 weight \*\*\*\* above-mentioned caprolactone denaturation hexa acrylate and a diluent monomer: The result of the test performed like 90 to 10 examples 1 is shown in Table 1.

[0064] The base material for the photographic printing papers was produced like the example 3 of example of comparison 4 comparison. However, in the constituent 8, the constituent 9 was prepared having used the mixed ratio of the above-mentioned caprolactone denaturation hexa acrylate and a diluent monomer as 75 to 25, and this was used instead of the constituent 8. The result of the test performed like the example 1 is shown in Table 1.

[0065] The base material for the photographic printing papers was produced like example of comparison 5 example 1. However, the electron ray hardenability organic compound-white-pigments mixing constituent for outermost layers of the following presentation (constituent 10) was prepared independently, and this was used instead of the constituent 1.

[0066] Constituent 10 \*\* Part Loadings 3 organic-functions urethane acrylate oligomer (trademark: NYU 60 weight section -frontier R-1301, Dai-ichi Kogyo Seiyaku make)

Titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) The result of the test performed like 40 weight sections examples 1 is shown in Table 1.

[0067] The base material for the photographic printing papers was produced like example of comparison 6 example 1. However, the electron ray hardenability organic compound-white-pigments mixing constituent for outermost layers of the following presentation (constituent 11) was prepared independently, and this was used instead of the constituent 1.

Constituent 11 \*\* Part Loadings Pentaerythritol tetraacrylate 60 weight sections (trademark: the beam set 710 and product made from the Arakawa chemistry)

Titanium dioxide (trademark: TIPAQUE A-220, Ishihara Sangyo make) The result of the test performed like 40 weight sections examples 1 is shown in Table 1.

[0068]

[Table 1]

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.ejje](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejje)

2006/11/30

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.ejje](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejje)

2006/11/30

項目	塗布液組成		塗 外 側 層		ヤマト試験
	塗外側層	内側層	水山の化合物中の カプロラクチン 残性アクリロイル 基の量(%)	水山の化合物と カプロラクチン との割合比率 (質量)	
実施例1	組成物1	組成物2	2	90:10	0.2
2	組成物3	-	2	75:25	0.7
3	組成物4	-	3	90:10	0.3
4	組成物5	-	3	75:25	0.7
比較例1	組成物6	-	0	90:10	0.3
2	組成物7	-	0	75:25	0.6
3	組成物8	-	6	90:10	1.9
4	組成物9	-	6	75:25	2.6
5	組成物10	-	0	100:0	9.2
6	組成物11	-	0	100:0	0.3

[0069]

[Effect of the Invention] The base material for the photographic printing papers of this invention makes it possible to make it possible to decrease sharply the xanthochroism of the general fault at the time of preparing an electron ray hardening resin layer, i.e., the paint film at the time of a development, and to hold flexibility, and is [ therefore ] practically very effective.

[Translation done.]